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(54) Title: SENSORS

(57) Abstract: There is disclosed a chemiresistor which comprises a non-conducting substrate at least partially coated with an electrically-conductive polypyrrole film, characterised in that the said substrate is a high melting-point, thermoplastic polymer selected from: an aromatic polyetherketone, a polyethersulphone, a polyetherimide, a polyimide and a polyamide. Also disclosed is a method of polymerizing a pyrrole monomer, comprising the step of contacting said pyrrole monomer with an oxidising agent in an aqueous solution, wherein the aqueous solution comprises an organic co-solvent which is at least partially miscible with water. There is also disclosed a process for treating a chemiresistor comprising a non-conducting substrate at least partially coated with an electrically-conductive polypyrrole film, wherein an oxidising agent or an acidic agent is contacted with the surface of the said film.

SENSORS

The present invention relates to a gas sensor and to a process for preparing such a sensor.

One type of known sensor comprises a gas sensitive-film coated on to a substrate. For example, sensors have been developed which employ conducting polymers capable of reversibly changing their electrical resistance in response to organic vapours. One example of such a conducting polymer is a polypyrrole.

GB-A-2234515 describes a process for preparing an electrically-conductive polypyrrole film on a non-conducting substrate which comprises contacting the substrate with pyrrole and an organic oxidising agent in a solvent (or with the colloidal polypyrrole that is the reaction product thereof) and removing the substrate while the film is at least substantially transparent. In this method the substrate may be brought into contact with the polymerising solution (or the resulting polypyrrole) by, for example dipping the substrate into a bath comprising the polymerising solution.

Known substrates include, glass, acrylic and polyester. Hitherto, low melting point thermoplastic materials, such as perspex have been preferred since the bonding of the polypyrrole film to the substrate can be enhanced by heating the substrate to the temperature at which it softens, followed by cooling. However, sensors based on a perspex substrate are usually sensitive to water and are therefore less sensitive at high humidities. They also tend to be unsuitable for use in conditions of variable humidity, and they can be unstable in air, causing the gas-sensitive film to degrade, known as "drift".

The present inventors have found that, when certain high melting-point, thermoplastic polymers

selected from polyetherketone, polyethersulphone, polyetherimide, polyimide and polyamide are used as the substrate with a conducting polymer film such as polypyrrole, the sensor has enhanced stability in air at room temperature, a reduced sensitivity to water, and an increased sensitivity for the target volatile, such as ammonia. Without wishing to be bound by theory, it is presently believed that these materials, as a result of their low permeability to water, low temperature coefficient of expansion and high glass transition temperature, are able to form a rigid platform for the conducting polymer film.

The inventors have also found that the stability in air can be increased further by the addition of an alcohol such as a lower alkyl alcohol, for example ethanol, to the polymerising medium used to prepare the substrate. This has also been found to increase the sensitivity of the sensor to alcohols.

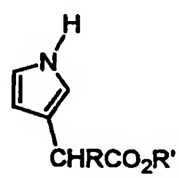
It has also been found that a post-treatment of the film, irrespective of the nature of the substrate, with an oxidising agent or acid results in increased responses to the target volatile.

Thus, according to a first aspect of the present invention, there is provided a chemiresistor which comprises a non-conducting substrate at least partially coated with an electrically-conductive polypyrrole film, characterised in that the said substrate is a high melting-point, thermoplastic polymer selected from: an aromatic polyetherketone, a polyethersulphone, a polyetherimide, a polyimide and a polyamide.

The substrate is preferably a thermoplastic aromatic polyetherketone substrate and may be crystalline or amorphous. A presently preferred substrate is polyetheretherketone (PEEK) as described, for example, in EP-A-0001879 which has been found to be very effective as a substrate for polypyrrole in

ammonia sensors.

The polypyrrole film is that prepared by or obtainable by polymerization of a pyrrole monomer, which includes pyrrole and substituted pyrroles, such as 3-substituted pyrroles. Examples of suitable 3-substituted monomers are those in which the 3-substituent is a an alkyl group, for example a substituted or unsubstituted alkyl group having up to 16 carbon atoms where the substituent is a carbonyl group, an ester group, an acid group or an amide group. Thus, examples of suitable 3-substituted polypyrrole monomers are:



where R and R' are independently hydrogen or lower alkyl.

More specifically, the chemiresistor of the invention may be produced by adding the pyrrole, or an aqueous solution of the pyrrole, with stirring, to an oxidising agent, for example, ferric ions. Without wishing to be bound by theory, it is believed that a colloidal suspension of polypyrrole results which may the be deposited or coated on the substrate when the substrate is contacted with the suspension. After a period which may be less than 3 hours, e.g. about 30 minutes, the coated substrate is removed, washed with water and dried, for example at ambient temperature. Reference is made here to GB-A-2234515. Where a substituted polypyrrole is desired, it is normally necessary to use a cosolvent, such as ethanol, to prepare the aqueous solution of the monomer.

Other methods for forming the polypyrrole film

exist, including electrochemical polymerization methods.

Contacts can be provided to the polypyrrole film by any of various methods, for example by the application of conducting paint. Alternatively, suitable contacts (for example gold) may be formed on the substrate prior to coating.

The resultant chemiresistor conducts electricity and the resistance changes reversibly in the presence of low concentrations of ammonia as well as other inorganic and organic species in the vapour phase. Unexpectedly, it was found that the use of a crystalline thermoplastic aromatic polyetherketone as the substrate resulted in a conducting polymer film with significantly enhanced stability in air at room temperature and under a range of humidities. The films exhibit a high sensitivity to ammonia, with a lower response to water vapour than films prepared on perspex.

According to a second aspect of the present invention, there is provided a method of polymerizing a pyrrole monomer, comprising the step of contacting said pyrrole monomer with an oxidising agent in an aqueous solution, wherein the aqueous solution comprises an organic co-solvent which is at least partially miscible with water.

During polymerization, the solution may be stirred.

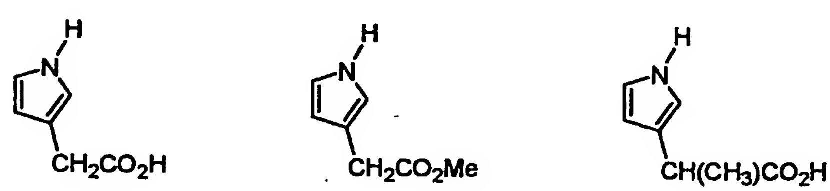
The organic co-solvent should ideally not be oxidisible by, or otherwise interfere with the oxidising agent, should not be attacked by high concentrations of hydrogen ions and should not interfere with the pyrrole monomer or polypyrrole product. Examples of suitable co-solvents are water soluble ethers, water soluble ketones such as lower (C1-6) alkyl ketones for example acetone, and water

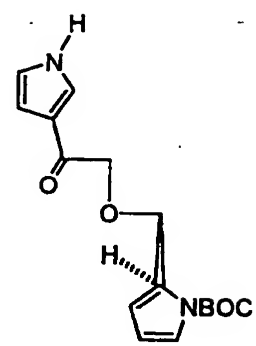
soluble alcohols (which are presently preferred) such as a lower (C1-6) alkyl alcohol, for example ethanol, as well as other water miscible solvents such as acetonitrile which have good solvent properties.

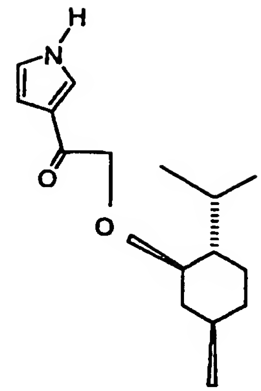
The proportion of co-solvent can be determined empirically. In the case of ethanol, an amount up to about 80% by volume may be used, although it is presently preferred to employ an aqueous ethanol solution containing from 10-30% v/v ethanol. In the case of acetonitrile, an amount up to 90% by volume may be used.

The oxidising agent is typically ferric ions and is typically used at a molar ratio of pyrrole to ferric ions of 1:n, where n is 2 or more.

The use of a co-solvent unexpectedly makes it possible to prepare conducting polymers from substituted pyrrole monomers, such as 3-substituted pyrroles, which are insoluble in water alone, and so opens up a range of new polypyrrole films with potentially valuable sensing properties. For example, the following 3-substituted pyrroles may be used in this aspect of the invention to prepare new polypyrrole sensors:







Without wishing to be bound by theory, it is believed that the method of this aspect of the invention results in a colloidal suspension of the polypyrrole. A chemiresistor may then be formed by contacting the suspension with a suitable non-conducting substrate which is preferably a crystalline thermoplastic aromatic polyetherketone, such as PEEK, as described above, although the other substrates mentioned above as well as other known substrates, such as glass, acrylic, polyester or perspex may be employed. After a period which may be less than 3 hours, e.g. about 30 minutes, the coated substrate is removed, washed with water and dried, for example at ambient temperature. Reference is again made here to GB-A-2234515.

It has also been found that the use of certain of the co-solvents in the polymerization step results in a polypyrrole which, when coated on a substrate to form a chemiresistor, gives a sensor with an increased sensitivity to that co-solvent as a species or molecule to be detected in the vapour phase. This has, in particular, been observed for the water soluble alcohols. It also gives enhanced sensitivity to species which are lower in the homologous series, i.e. where the molecule has a lower cross-sectional area. Suitable water-soluble alcohols are the lower C1-6 alcohols for example methanol, ethanol, propanol (all

isomers), butanol (all isomers). Thus, the use of an ethanol co-solvent results in a sensor having increased sensitivity to ethanol and also to methanol. It is theorised that the use of an alcohol co-solvent leads to the formation of "pores" or "channels" in the film which are so-shaped as to absorb the same alcohol molecule (or ones smaller than it) from the vapour phase in use as a sensor, leading to an enhanced response.

According to a third aspect of the invention, there is provided a process for treating a chemiresistor comprising a non-conducting substrate at least partially coated with an electrically-conductive polypyrrole film, wherein an oxidising agent or an acidic agent is contacted with the surface of the said film.

The polypyrrole film may be one prepared in accordance with the methods described herein or by other methods which may be known per se. The polypyrrole film may be one prepared by polymerising a pyrrole monomer or a substituted pyrrole monomer.

The treated chemiresistor prepared in accordance with this aspect of the invention exhibits significantly superior electrical resistance changes to ammonia, while maintaining low degradation/drift in air.

The acidic agent may be an aqueous solution of a mineral acid such as hydrochloric acid, nitric acid or sulphuric acid, with hydrochloric acid being presently preferred. In addition, strong organic acids are also suitable, such as CF_3COOH or HCOOH. The acidic solution may be applied to the film at a concentration and for a time sufficient to increase the electrical resistance of the film when exposed to ammonia. For example, where the acidic agent is hydrochloric acid, good results were achieved using 6M HCl treatment for 40

minutes.

Without wishing to be bound by theory, it is presently believed that the acid treatment results in protonation of the polypyrrole resulting in more positive charges on the polymer. The increased concentration in positive charges may produce an increased concentration of binding sites for nucleophiles such as ammonia and other amines.

The oxidising agent may be a solution of metal ions, such as a solution of ferric ions and may be applied by way of a solution having a concentration of, for example 0.1M. Other oxidising agents such as hydrogen peroxide are also contemplated. The oxidising agent may be applied to the film at a concentration and for a time sufficient to increase the electrical resistance of the film when exposed to ammonia.

Again, without wishing to be bound by theory, it is believed that the oxidising agent may oxidise the polymer and increase the concentration of positive charges, hence mirroring the effect of acid. The oxidising agent treated films also show an enhanced response to nucleophiles.

For a better understanding of the present invention, and to show how the same may be put into effect, reference will now be made, by way of example only, to the following examples.

EXAMPLES

In these examples, the following film synthesis methodology was used.

PEEK strips 1 cm wide are prepared, and rinsed with ethanol and then distilled water. For films prepared in aqueous ethanol solutions, a final rinse with the ethanol solution used in the synthesis is also carried out. The PEEK strips are placed in the polymerisation bath orthogonal to the liquid surface, the time allowed for the polymerisation being

determined by the additives present in the polymerisation solution. For the preparation of polypyrrole films in aqueous solution without the presence of additives, polymerisation times of between 10 minutes and 1 hours are typical; for the preparation of polymer films in aqueous ethanol solutions, and in aqueous solutions of 2-butanol or butane-1,3-diol, polymerisation times of between 1 and 4 hours are appropriate.

Once prepared, the films are rinsed thoroughly with distilled water. Films obtained in aqueous solution, and aqueous ethanol solution, are allowed to dry in air for 24 hours, as were films which had been subjected to subsequent oxidation or treatment with acid; films prepared in aqueous 2-butanol and butane-1,3-diol solutions are dried for 6 hours under vacuum at 70°C to remove residual alcohol from the matrix of the polymer. Films which are to be subjected to further modification with acid or iron (III) salts are not dried prior to the treatment.

Sensors are prepared by cutting the polymer coated PEEK strips into 1 cm squares, removing the film from one side of the square with gentle abrasion, and mounting the square, film side uppermost, on a strip of Veriboard. Electrical contacts between the film and the Veroboard mount are made with silver conductive paint. Sensors thus prepared are allowed to stabilise for at least 24 hours prior to exposure to vapours.

Testing of the sensors to analyte vapours is carried out at room temperature. The initial sensor baseline resistance in ambient air is measured (R_b). The sensor is then exposed to the analyte vapour for 300 seconds; the sensor resistance at the end of this time being noted (R_v). Percentage responses for the sensors to analyte vapours are calculated using the relation :

$$\% \text{ response} = [(R_v - R_b)/R_b] \times 100.$$

Sensors are exposed to organic headspace vapours by placing the sensor in a sealed vessel containing a saturated vapour of the analyte. For exposure of the sensors to lower concentrations of organic vapours, a known mass of the analyte is volatalised in a sealed vessel of known volume, and dilutions of the vapour made to achieve the required vapour concentration. For exposure of the sensors to ammonia vapour, the sensors were placed in a sealed vessel over aqueous solutions of ammonia with known ammonia concentrations in the vapour phase.

Example 1

Iron (III) nitrate nonahydrate (1.87 g) was dissolved with stirring in de-ionised water (45 cm^3). To this was added an aqueous solution of pyrrole (0.019 g in 5.0 cm^3 of de-ionised water). PEEK strips were placed in the polymerisation solution for between 10 minutes and one hour. Films of good conductivity were obtained. The average resistance of sensors prepared from a polypyrrole film obtained after a polymerisation time of 1 hours is given in Table 1.

Table 1

Average resistance (5 sensors) (MΩ)	Coefficient of variation (%)	Range (MΩ)
0.497	22	0.303-0.636

The film properties may be adjusted by variation of the polymerisation time; similar results may be

achieved by alteration of the molar concentrations of the reacting species, and the ratio of pyrrole to oxidant.

Example 2

Polypyrrole films on PEEK were prepared using the above method, in aqueous ethanol solutions rather than in de-ionised water (with pyrrole initially dissolved in the appropriate solvent system). For ethanol concentrations of 50 % v/v and less, films are obtained at all polymerisation times (1 hour to 4 hour). At higher ethanol concentrations, films are obtained only at the longer polymerisation times. No films are obtained with ethanol concentrations of 80 % v/v and above. For the preparation of sensors, films prepared with ethanol concentrations of 30 % v/v and less are most suitable, owing to their relatively high conductivities. The resistance values for polypyrrole sensors prepared in aqueous ethanol solutions of between 10 and 30 % v/v ethanol are given in Table 2.

Table 2

Ethanol concentration (% v/v)	Average sensor resistance (4 sensors) (MΩ)	Coefficient of variation (%)	Range (MΩ)
10	1.288	14	1.108-1.626
20	7.409	10	6.566-8.412
30	26.16	38	9.507-38.40

There is a marked increase in sensor resistance with increased ethanol concentration; however there is no clear trend in the variation in sensor resistance with increasing polymerisation time for a given ethanol concentration in the polymerisation medium.

The ageing characteristics of films prepared in 10 % v/v aqueous ethanol solution are presented in Figure 1 (sensor1 - polymerisation time 1 hour, sensor2 - polymerisation time 2 hours). Sensor1 shows a marked

stability, with no discernible increase in resistance over the 30 days of testing. Similar stabilities are observed for polypyrrole films prepared in 20 % v/v ethanol solutions, for polymerisation times of 3 hours or less.

In addition, polypyrrole sensors prepared in aqueous ethanol solution show markedly greater responses to certain analyte vapours than sensors prepared in aqueous solution. The responses of a polypyrrole sensor prepared in aqueous solution (sensor0) and a sensor prepared in 20 % v/v ethanol solution (sensor3), polymerisation time for both sensors being 1 hour, to D-(+)-α-methylbenzylamine and ethanol headspace are presented in Table 3.

Table 3

Headspace vapour	Sensor response (%)	
	Sensor0	Sensor3
D-(+)-α-methyl benzylamine	+22.5	+37
Ethanol	+1.9	+2.3

Example 3

This example relates to the post-treatment of polypyrrole films, on PEEK or perspex. Subsequent acid treatment of the polypyrrole films on PEEK is carried out by placing them in an aqueous solution of hydrochloric acid (18 % wt/v) for 40 minutes, followed by rinsing of the films with de-ionised water and drying in air. The procedure may be adjusted by varying the acid used; the concentration of the acid, and the time of treatment (typically from 15 minutes to 20 hours).

Subsequent treatment of the polypyrrole films on PEEK with oxidising agents may be carried out by placing them in a solution of iron (III) nitrate nonahydrate (30 g) in de-ionised water (300 cm^3) for 40

minutes, followed by rinsing the films with de-ionised water and drying in air. The procedure may be adjusted by varying the oxidant used; the concentration of the oxidant, and the time of treatment (typically from 15 minutes to 20 hours).

CLAIMS:

1. A chemiresistor which comprises a non-conducting substrate at least partially coated with an electrically-conductive polypyrrole film, characterised in that the said substrate is a high melting-point, thermoplastic polymer selected from: an aromatic polyetherketone, a polyethersulphone, a polyetherimide, a polyimide and a polyamide.

2. A chemiresistor according to claim 1, wherein the substrate is a thermoplastic aromatic polyetherketone substrate.

3. A chemiresistor according to claim 2, wherein the substrate is polyetheretherketone (PEEK)

4. A chemiresistor according to any preceding claim, wherein the polypyrrole film is that prepared by or obtainable by polymerization of a pyrrole monomer.

5. A chemiresistor according to claim 4, wherein the polypyrrole film is prepared by polymerization of pyrrole or a substituted pyrrole.

6. A chemiresistor according to claim 5, wherein the substituted pyrrole is a 3-substituted pyrroles.

7. A chemiresistor according to any preceding claim, substantially as herein exemplified.

8. A gas sensor comprising a chemiresistor according to any preceding claim.

9. A method of polymerizing a pyrrole monomer, comprising the step of contacting said pyrrole monomer with an oxidising agent in an aqueous solution, wherein the aqueous solution comprises an organic co-solvent which is at least partially miscible with water.

10. A method of polymerizing a pyrrole monomer according to claim 8, wherein the co-solvent is selected from water soluble ethers, water soluble ketones, water soluble alcohols and acetonitrile.

11. A method of polymerizing a pyrrole monomer according to claim 10, wherein the co-solvent is

ethanol or acetonitrile.

12. A method according to claim 9, 10 or 11, wherein the pyrrole monomer is pyrrole or a substituted pyrrole.

13. A method of polymerizing a pyrrole monomer according to claim 9, 10, 11 or 12, wherein the oxidising agent is a solution of ferric ions.

14. A method according to claim 9, substantially as exemplified herein.

15. A process for preparing an electrically-conductive polypyrrole film on a non-conducting substrate, which comprises contacting the substrate with an aqueous solution comprising a pyrrole monomer and an oxidising agent, wherein the aqueous solution comprises an organic co-solvent which is at least partially miscible with water.

16. A process according to claim 15, wherein the pyrrole monomer is pyrrole or a substituted pyrrole.

17. A process according to claim 15 or 16, wherein the co-solvent is selected from water soluble ethers, water soluble ketones, water soluble alcohols and acetonitrile.

18. A process according to claim 15, 16 or 17, wherein the co-solvent is ethanol or acetonitrile.

19. A process according to claim 15, 16, 17 or 18, wherein the oxidising agent is a solution of ferric ions.

20. A chemiresistor prepared by the process according to any one or more of claims 15 to 18.

21. A process according to claim 15, substantially as exemplified herein.

22. A gas sensor comprising a chemiresistor according to claim 20.

23. A process for treating a chemiresistor comprising a non-conducting substrate at least partially coated with an electrically-conductive polypyrrole film, wherein an oxidising agent or an acidic agent is contacted with the surface of the said film.

24. A process according to claim 23, wherein the surface of the film is contacted with an acidic agent which is an aqueous solution of a mineral acid or a strong organic acid.

25. A process according to claim 23 or 24, wherein the acidic solution is applied to the film at a concentration and for a time sufficient to increase the electrical resistance of the film when exposed to ammonia.

26. A process according to claim 23, wherein the surface of the film is contacted with an oxidising agent which is applied to the film at a concentration and for a time sufficient to increase the electrical resistance of the film when exposed to ammonia.

27. A process according to claim 23, substantially as exemplified herein.

28. A treated chemiresistor prepared by the process according to claim 23, 24, 25 or 26.

29. A gas sensor comprising a chemiresistor according to claim 28.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 00/04012

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 821 228 A (HUGHES AIRCRAFT CO) 28 January 1998 (1998-01-28) page 5, line 17; claim 4 ---	1,8,9, 15,20, 22,23, 28,29
Y	EP 0 411 793 A (BRITISH AEROSPACE) 6 February 1991 (1991-02-06) page 2, line 41 - line 42; claim 5 ---	1,8,9, 15,20, 22,23, 28,29
A	EP 0 267 392 A (ROCKWELL INTERNATIONAL CORP) 18 May 1988 (1988-05-18) abstract ---	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search	Date of mailing of the international search report
15 March 2001	23/03/2001

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PEARCE T C ET AL: "ELECTRONIC NOSE FOR MONITORING THE FLAVOUR OF BEERS" ANALYST, GB, LONDON, vol. 118, no. 4, 1 April 1993 (1993-04-01), pages 371-377, XP000196878 table 1	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 00/04012

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